# Development of Efficient UV-LED Phosphor Coatings for Energy Saving Solid State Lighting

**Final Report**

**Reporting Period:**
**January 2004 - May 2006**

**Uwe Happek**

**Report issued:**

**January 2007**

**DE-FC26-04NT41956**

**The University of Georgia**
**Department of Physics and Astronomy**
**Athens, GA 30602-2451**

**Sub-Contractor:**

**Dr. Anant Setlur**

**GE Global Research Center**
**Niskayuna, NY 12309**

## DISCLAIMER

## ABSTRACT

The University of Georgia, in collaboration with GE Global Research, has investigated the relevant quenching mechanism of phosphor coatings used in white light devices based on UV LEDs. The final goal of the project was the design and fabrication of a high-efficacy white light UV-LED device through improved geometry and optimized phosphor coatings.

At the end of the research period, which was extended to seamlessly carry over the research to a follow-up program, we have demonstrated a two-fold improvement in the conversion efficiency of a white light LED device, where the increase efficacy is due to both improved phosphor quantum efficiency and lamp geometry. Working prototypes have been displayed at DOE sponsored meetings and during the final presentation at the DOE Headquarters in Washington, DC.

During the first phase of the project, a fundamental understanding of quenching processes in UV-LEDs was obtained, and the relationships that describe the performance of the phosphor as a function of photon flux, temperature, and phosphor composition were established. In the second phase of the project, these findings were then implemented to design the improved UV-LED lamp. In addition, our research provides a road map for the design of efficient white light LEDs, which will be an important asset during a follow-up project led by GE.

## Table of Contents

# INTRODUCTION

The development of efficient solid state lighting (SSL) sources by 2020 will enable the reduction in annual lighting energy consumption for an annual savings of 0.74 quadrillion BTUs (quads). The acceptance of SSL sources will require complete flexibility in choosing the color temperature (CCT) and color rendering index (CRI) of the white light source. This can be achieved using a combination of UV-LEDs with phosphors that down-convert UV-LED radiation into visible light. The color of these lamps is completely controlled by the selection of appropriate phosphors, giving the required control over lamp color for many general illumination applications. However, achieving this goal will require the optimization of all aspects of the white LED lamp, including the phosphor efficiency.

In typical linear fluorescent lamps, the phosphor conversion (from Hg radiation) efficiency is greater than 80%. However, in typical white LEDs, the phosphor conversion efficiency (from either blue or UV LED radiation) ranges from 40-60% depending upon the LED package and the phosphor selection. The goal of this program is to determine the fundamental causes of this lower phosphor conversion efficiency and to improve this efficiency by addressing these causes, either though phosphor or LED package design. The eventual goal for UV-LED phosphors is to match or exceed the conversion efficiency of typical fluorescent lamp coatings. Our effort can be summarized by the selection and evaluation of appropriate UV-LED phosphors, testing of these UV-LED phosphors in typical LED packages, identifying the phosphor quenching mechanisms within these packages, and fabricating improved LED lamps using the fundamental knowledge of quenching mechanisms.

EXECUTIVE SUMMARY

The development of energy efficient solid state lighting based on phosphor coated UV-LEDs was outlined as a focused eighteen month project, because we found that the large fraction of the U.S. energy consumption for lighting (14 percent) necessitates the rapid development of energy efficient lighting that could replace the standard incandescent lamp. During the course of our project, the price for crude oil more than doubled, and with it has risen the relevance of our project.

Among the different avenues for solid state lighting we have chosen the combination of UV-LED and phosphor coating, hereby duplicating the successful concept of gas-discharge based fluorescent lighting (Fig. 1). Compared to standard fluorescent lighting phosphors, the conditions for UV-LED phosphors are extreme, due to the high photon flux and elevated temperatures in high power devices, and so-called quenching phenomena must be avoided in order to achieve energy efficient lighting.

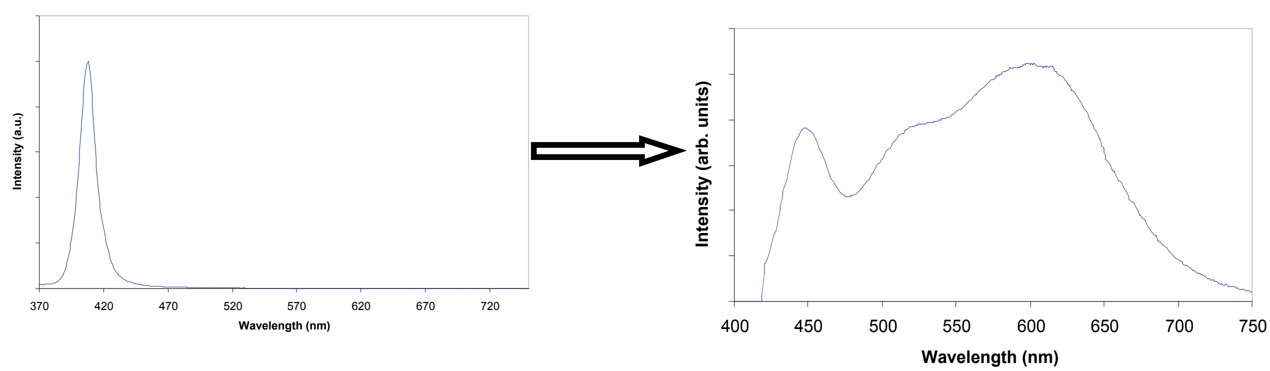



Fig.1: Concept of UV-LED based white light generation.

To achieve this goal, the team included both material chemists from industry with an extensive background in phosphor materials and university based physicists specialized in solid state physics and luminescence.

In order to increase the efficacy of current devices, first an understanding of the fundamental processes in a phosphor material under conditions relevant to LED operation is needed. Task 1, the selection and synthesis of phosphors, and Task 2, the initial evaluation of the phosphors, were coupled in a feedback loop, i.e. often the experimental results stimulated the production of modified materials. Important in this context is the application of an experimental technique to identify ionization processes in phosphor materials (see section on Experimental Techniques). After the characterization of the bulk phosphor, prototype LED devices were fabricated (Task 3) and studied under standard (Task 3) and extreme (Task 4) conditions.

The findings of Task 3 and Task 4, which included the observation of substantial quenching under extreme LED conditions due to high photon flux, were use to develop design rules for improved LED phosphor coatings, and ultimately led to the fabrication of an UV-LED based lamp with a two-fold improved phosphor conversion efficiency.

Several prototypes were manufactured and demonstrated both at a DOE sponsored workshop on solid state lighting in Orlando, Florida and at the final presentation and de-briefing at the DOE headquarters in Washington, DC. In addition, a device was provided to the Department of Energy.

Major aspects of this program had been subcontracted from the University of Georgia. The identification and synthesis of optimized phosphors was subcontracted to GE Global Research using various GE proprietary phosphor compositions. In addition, the fabrication of all LED lamps had also been subcontracted to GE Global Research.

Within the present project, we have focused our attention on ionic phosphor materials. Most recently, broad band emitting covalent materials like sulfides and nitrides have been proposed for solid state lighting applications. We have used a no-cost extension of our project to perform initial studies on these materials and to conduct experiments for a follow-up project, in order to rapidly develop even more efficient solid state lighting sources based on UV LEDs.

## EXPERIMENTAL TECHNIQUES

The arsenal of experimental techniques available include the entire range of optical characterization, from emission spectroscopy using CCD equipped spectrographs (five), photoexcitation, and photon-counting techniques to study relaxation phenomena. The photon counting equipment includes multichannel scalers with a time resolution of 1 nsec, higher temporal resolution can be achieved with time-to-Amplitude converters.

The excitation, emission and relaxation measurements are being performed at a large range of temperatures, necessary to establish temperature induced quenching phenomena. In addition to standard cryostats (eight) a "high temperature" cryostat was essential for varying the sample (phosphor) temperature between 10K and 500 K.

Prototype LEDs were investigated by monitoring the emission spectrum and intensity as a function of input power. For investigations of transient phenomena, the LEDs were pulsed with a nsec pulse generator.

The original proposal included the utilization of ruby powder to measure the temperature distribution within the device. It turned out to be more practical, efficient, and less intrusive to use the temperature dependence the relaxation properties of the actual phosphor to monitor the phosphor layer temperature.

In terms of specialized techniques, we use Thermally Stimulated Luminescence Excitation Spectroscopy (TSLES) to identify photo-ionization processes in the phosphors. Photo-ionization is an important quenching mechanism; in addition, it can lead to long-term degradation of the phosphor material. This technique is exclusively used by our group, and has been developed with previous DOE funding.

In order to expedite the measurements, we have improved the TSLES technique by using infrared radiation instead of heat, resulting in Infrared Stimulated Luminescence Excitation Spectroscopy (ISLES). The goal of TSLES and ISLES is the measurement of the ionization threshold of an optically active ion in a phosphor material. Ionization in this case is equivalent to promoting an electron from an optically active ion to the host conduction band. To observe the ionization process, we make use of so-called traps, which are ubiquitous in any host material and trap electrons that are promoted to the conduction band of the host. (See Fig. 2) The trapped electrons can either be liberated by applying heat to the sample, (in the case of TSLES) or infrared radiation (in the case of ISLES). In both cases the liberated electron recombine with the optically active ions and emit luminescence, thus the expressions "Thermally Stimulated Luminescence" or "Infrared Stimulated Luminescence". We converted these physical effects into a spectroscopic technique by illuminating the samples at various wavelength and probe whether traps have been filled either via heat or infrared radiation. If the energy of the photons is insufficient to promote electrons to the conduction band, no traps can be filled, and there will be no thermally or infrared stimulated luminescence. However, if the photon energy is sufficient to promote electrons to the conduction band (i.e. if the photon energy is equal to or larger than the ionization threshold), thermally or infrared induced luminescence will be observed. Finally, a plot of the integrated stimulated luminescence as a function of excitation wavelength will provide the ionization energy of the optically active ion in a phosphor material.

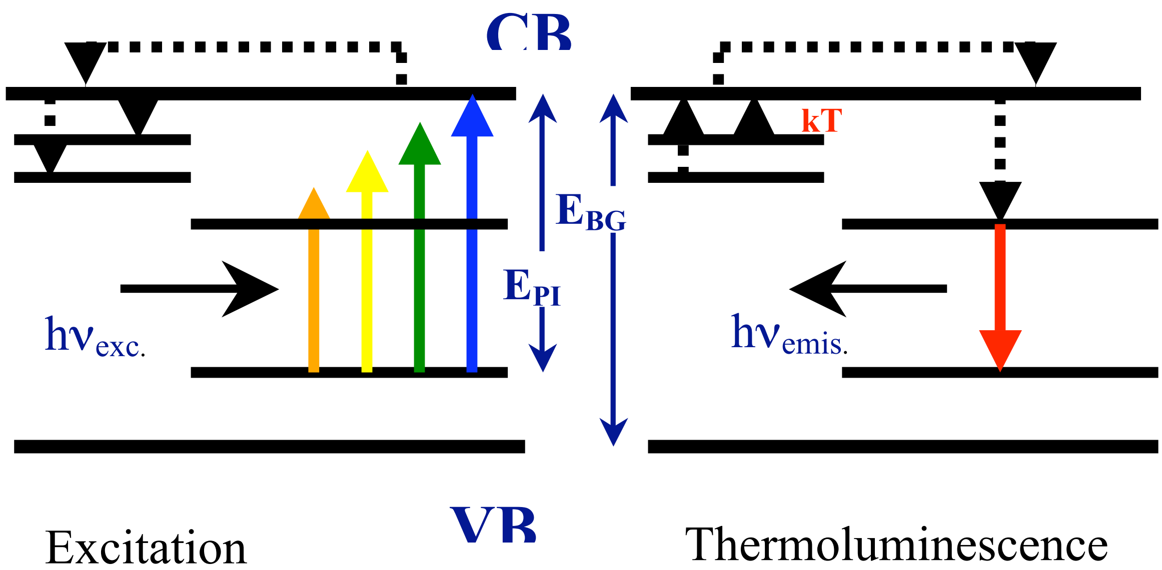



Fig. 2: Principle of Thermoluminescence

The advantage of ISLES over TSLES is the speed in which the experiment can be conducted: emptying the traps via infrared radiation can be achieved within seconds, while TSLES requires several minutes to ramp the temperatures to several hundred degrees, followed by a long cool-down period of again several minutes.

## RESULTS AND DISCUSSIONS

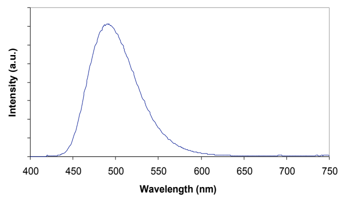
The project was structured into 6 Tasks, with Task 1 through Task 5 being part of the actual research effort, and Task 6 dealing with the program management (Fig. 3).

| Program Activities | Year 1 | | | | Year 2 | | Deliverables |
|---|---|---|---|---|---|---|---|
| | Q1 | Q2 | Q3 | Q4 | Q5 | Q6 | |
| Task 1 Synthesis of optimized LED phosphors for bulk studies. | | | | | | | • Rationale for the selection of UV-LED phosphors to be studied in this program (Q2).<br>• Synthesis of sufficient quantities of UV-LED phosphors for study in this program (Q2). |
| Task 2 Evaluation of luminescence properties of bulk phosphors. | | | | | | | • Optical characterization data relating to the basic luminescent properties and luminescent quenching mechanisms of UV-LED phosphors in bulk form (Q2). |
| Task 3 Fabrication and initial evaluation of prototype LED devices. | | | | | | | • Fabrication of phosphor coated UV-LED prototypes for study in this program (Q2).<br>• Evaluation of typical UV-LED phosphors in typical UV-LED packages (Q2). |
| Task 4 Evaluation of phosphor coatings in the LED package. | | | | | | | • Optical characterization of the phosphor coatings during normal and extreme LED operation (Q6).<br>• Determine the fundamental quenching mechanisms for phosphor coatings within UV-LEDs (Q6). |
| Task 5 Development of optimized LED packages for higher efficacy LEDs. | | | | | | | • Design rules for UV-LED phosphor coatings (Q6).<br>• Improved LED package design that will reduce phosphor quenching due to phosphor/ LED package interactions (Q6).<br>• Fabrication of improved phosphor coated UV-LED prototypes (Q6). |
| Task 6 Program management. | | | | | | | |

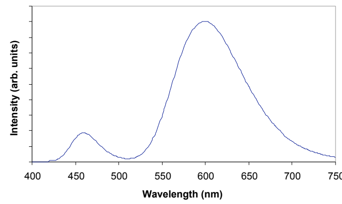
Fig. 3: List of tasks and milestones.

The first task was carried out at the GE Corporate Research Center. Our GE collaborators took the lead in selecting promising UV-LED phosphors and also synthesized sufficient amounts of materials needed to complete the other tasks of this program. The materials provided included both simple and advanced phosphor blends (Fig. 4). Important to note is the fabrication of D55/D65 blends for the UV-LED-Phosphor platform (See Task 2)

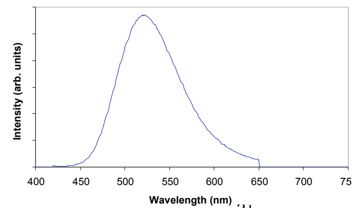
In order to achieve a fundamental understanding of the complex energy relaxation and energy transfer processes, single phosphor materials were provided as well. Moreover, in order to unravel the role of the activator concentration on the phosphor performance, concentration series were synthesized for a number of relevant materials.



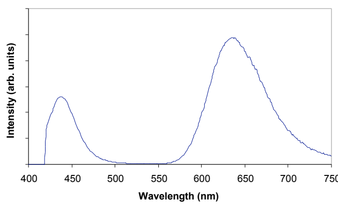

$Sr_4Al_{14}O_{25}:Eu^{2+}$



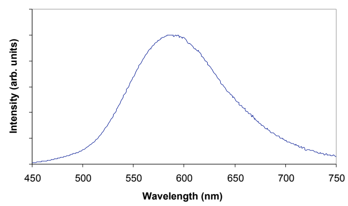

$Ca_5(PO_4)_3Cl:Eu^{2+},Mn^{2+}$



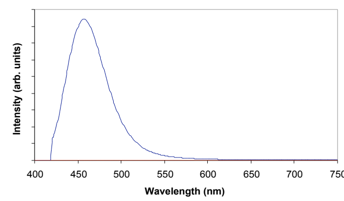

$SrAl_2O_4:Eu^{2+}$




$Sr_3MgSi_2O_8:Eu^{2+},Mn^{2+}$




$(Sr,Ca)_2SiO4:Eu^{2+}$

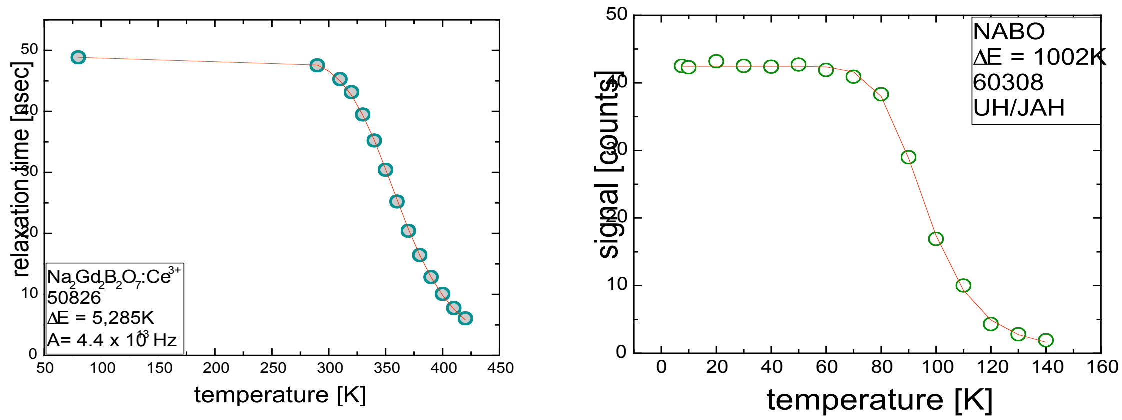



$Sr_5(PO_4)_3Cl:Eu^{2+}$

Fig.4: Examples of phosphor materials provided by GE Global Research.

Task 2 included the optical evaluation of the bulk phosphors, i.e. photoexcitation, emission, and relaxation measurements for the single activator phosphors, and energy transfer studies for complex phosphor blends. In order to understand the complex absorption, emission and energy transfer processes in a phosphor blend, single phosphors were investigated in detail, including investigation of phosphors with different doping levels in order to distinguish single ion phenomena from collective ones.

Important with respect to Task 2 was the quantification of quenching parameters, i.e. the quenching temperature (Fig. 5). In order to distinguish between level crossing and photoionization as the source of thermal quenching, thermally stimulated luminescence excitation spectroscopy (TSLES) as well as infrared stimulated luminescence excitation spectroscopy (see section on Experimental Techniques) were performed at UGA.




**ΔE = 3700 cm$^{-1}$ (0.46 eV)** **ΔE = 700 cm$^{-1}$ (0.09 eV)**

Fig. 5: Thermal Quenching of the two activator sites in NABO

These measurements lead to an energy level diagram that includes both the electronic level of the activator ion and the host energy bands (Fig. 6).

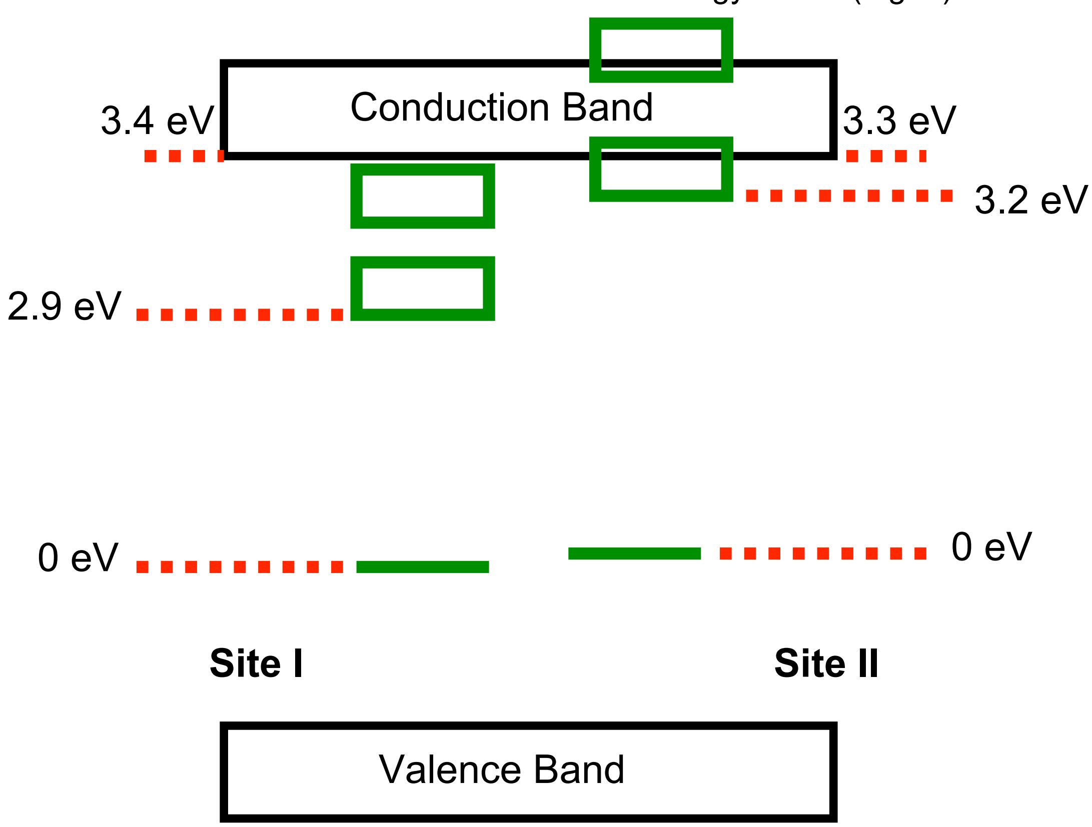



Fig. 6: Energy Diagram for the two activator sites in NABO.

As part of this task, D55/D65 spectra have been demonstrated and quenching mechanisms have been quantified (Fig. 7).

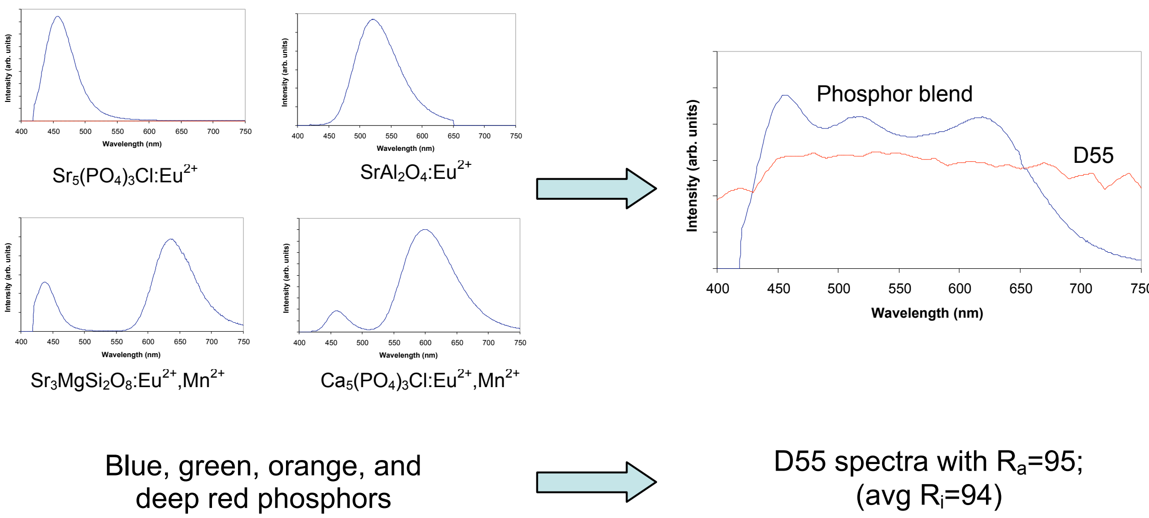



Fig. 7: Demonstration of D55 Spectra.

During the fundamental evaluation of phosphor materials, the UGA measurements gave clear evidence that the low quantum efficiency of specific materials synthesized by GE Global Research was due to non-optimized synthesis procedures, instead of intrinsic quenching mechanisms. This critical information was then used in internally funded GE Global Research and GELcore programs to develop a key phosphor for GELcore's white light prototypes and future products.

Based on the findings of Task 2, prototype LED devices were fabricated at the GE Corporate Research Center in Task 3 and evaluated both at GE and UGA. Important aspects of this task were the monitoring of the emission spectrum in the LED package and the use of the LED chip to perform time-resolved measurements on the phosphor materials via pulsed operation of the LED. Extensive studies of quenching of the emission as a function of LED power were carried out, where the optical quenching was also compared to the observed decrease in the relaxation time of the optical activators within the phosphor materials.

Quenching studies were carried out under extreme conditions (Task 4), which is an important aspect of this research, due to the rapid development of LED chips with increasing flux density. During these studies, we have observed strong non-linearities in the lumens vs. power dependence (Fig. 8).

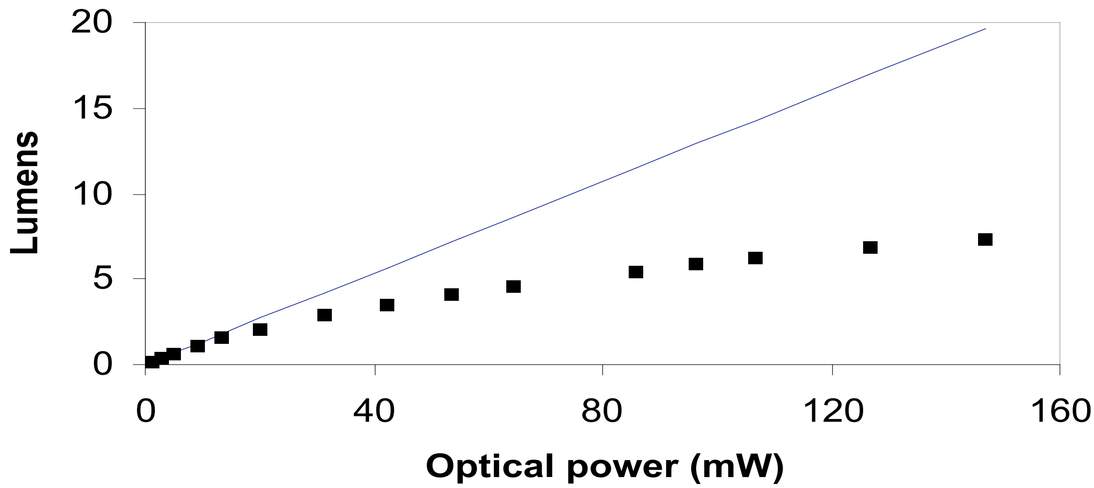



Fig. 8: Nonlinear power dependence of lumen output.

In some materials, the non-linearities are due to the increased temperature, while in others the large photon flux leads to a bottle neck. Using temperature dependent phosphor properties (relaxation time, energy transfer rate) we were able to evaluate the temperature in situ, and we could separate the effect of temperature from that of the photon flux.

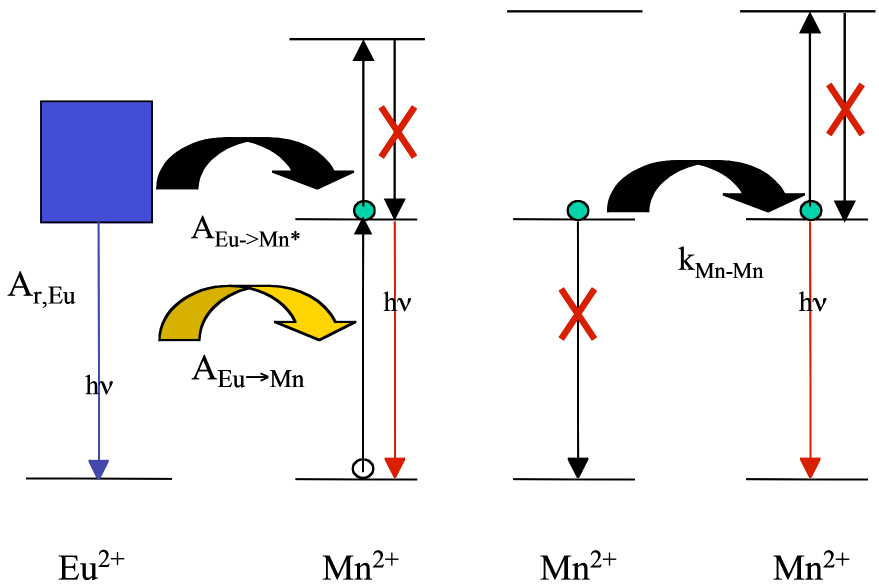



Fig.9: Energy transfer model for a $Eu^{2+}$ - $Mn^{2+}$ system

This, then, allowed us to develop design rules of optimized LED packages for higher efficacy LEDs (Task 5). The spectroscopic characterization (emission spectra, decay time, rise time, thermoluminescence) of the GE proprietary phosphors during LED operation, gave us a clear picture of the quenching mechanisms for these phosphors in LED packages(Fig. 9).

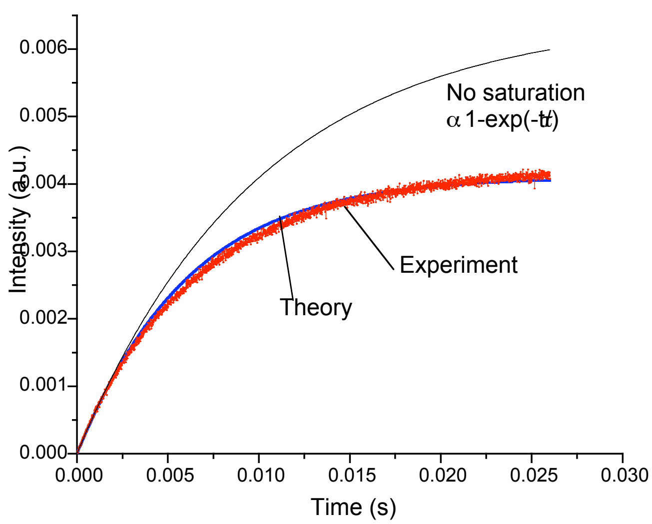



Fig. 10: Comparison between model (blue) and experiment (red)

Specifically, we obtained the relevant parameters regarding thermally or flux induced quenching, radiative lifetime, and the energy transfer rate between a pair of ions.

The actual design of the white light LED device must depend on the properties of the phosphors used. For example, if strong thermal quenching is observed, the improved design could involve moving the phosphor layer away from the LED chip or different thermal management schemes for the phosphor layer. Other modifications of the phosphor coatings in the LED package must also be considered depending upon the phosphor performance and spectroscopy.

The final deliverable included in Task 5 was the actual production of a high efficacy LED device with excellent color rendering (Fig. 11). Two types of improved LED devices were presented, one at the DOE sponsored LED workshop in Orlando, Florida (2006), the other at the final project presentation at the DOE Headquarters in Washington, DC. Optimized geometry and improved phosphor materials resulted in an improvement of the efficacy by a factor of 4, as compared to the initial GELcore white light LED., and a color rendering index of 80+, combined with a color temperature of 3500 K to 4100K. As can be seen in Table 1, the increased phosphor efficiency accounts for about 60% of the efficacy gain.

We find it important to note that scalable packages can be produced with outputs between 40 lms and 1000 lms, without sacrifices with respect to efficacy or color rendering.

| **Initial Violet LED+Phosphor Lamps** | **New Phosphor Systems+Package Design** |
|---|---|
| CCT ~ 3500-4100K, CRI~80 | CCT ~ 3500-4100K, CRI~80+ |
| Phosphor conv. eff. ~ 35-40% | Phosphor conv. eff. ~ 65-70% |
| Chip WPE ~ 11% | Chip WPE ~ 23% |
| Efficacy ~ 8-10 lm/W | Efficacy ~ 35 lm/W |

Table 1: Comaprison between initial and final lamp performances.

Important for the successful completion of our project was the close collaboration of the UGA and GE teams. Weekly phone conferences were held to discuss the current and upcoming tasks, in addition to hundreds of e-mails and additional phone calls. The collaboration was flawless, as an example, samples requested by UGA were synthesized and delivered in less than a week.

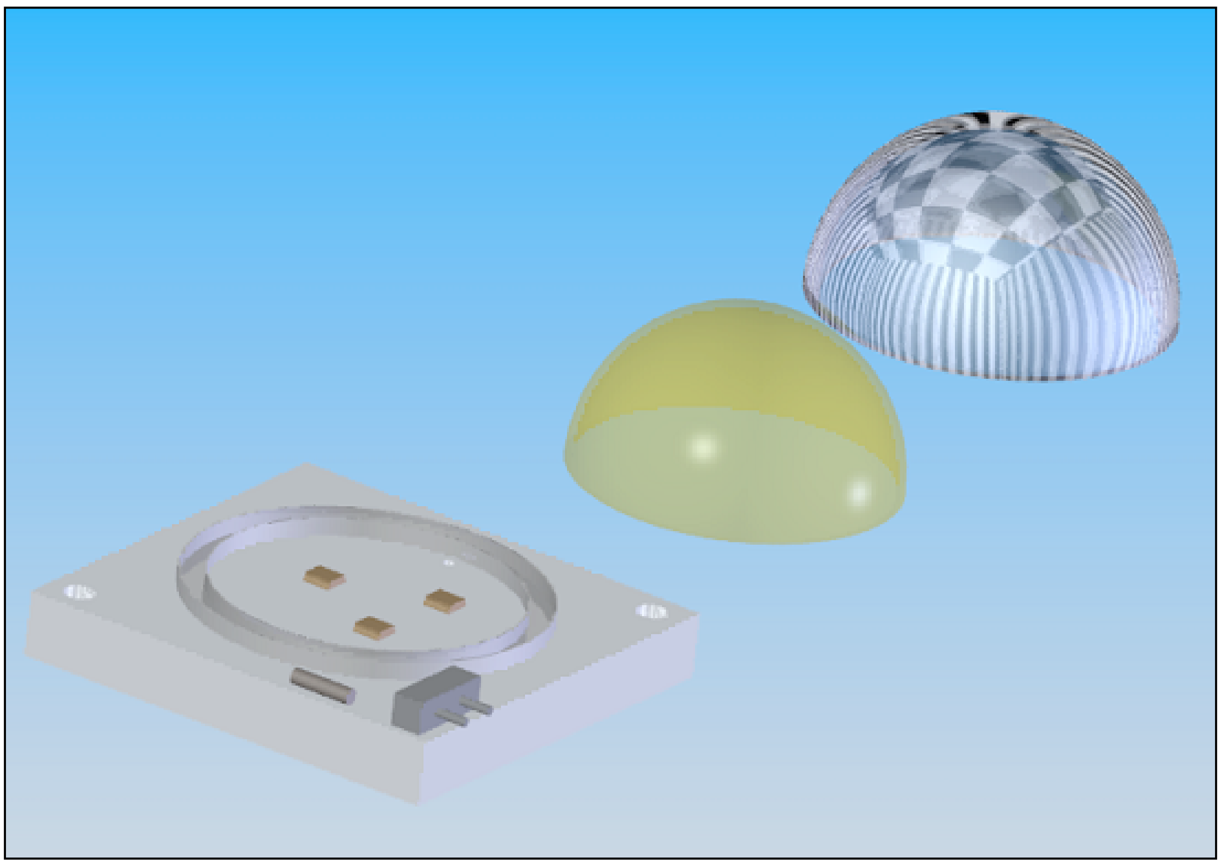


Fig. 11: LED lamp design.

We like to note the educational aspect of the project, two students J. Fleniken and B. Wen) graduated during the project, and a third (P. Schmidt) graduated three months after the project ended.

## CONCLUSIONS

The need for energy efficient lighting increases with the cost of energy, and the recent explosion of crude oil prices have made this project even more important than it was a the beginning of our studies. Energy efficient lighting inevitably involves lighting products that are attractive to the consumer - the most efficient product will not save energy if it is not used. Based on this point of view, UGA and GE studied solid state white lighting devices that are based on UV-LEDs. This approach decouples the excitation source (the UV-LED) and the emission in the visible range, which is entirely due to the phosphor coating. The advantage of this approach lies in the complete flexibility regarding color rendering and color temperature.

The goal of this project was the demonstration of an improved LED device, and the path to achieve this was not trial and error but a systematic study of the relevant properties of a variety of promising phosphor materials and how the individual phosphors perform under the extreme conditions of UV-LED excitation. Furthermore, we investigated the origin of thermal and/or flux quenching, which will aid the design of improved phosphor materials in the near future.

The experimental results were then used to establish design rules for the development of efficient white light LED devices. As the final step, two designs of high quality lighting (CRI~80+, CT ~ 3500 -4100K) were demonstrated that showed a 3.5 - 4 fold increase of efficacy over initial GELcore lamps. An important factor was the increase of phosphor conversion efficiency by almost a factor of two. The final lamp design can be used for scalable packages between 40 lms and 1000 lms, without sacrifices in CCT, CRI, or phosphor conversion efficiency.

Beyond the demonstration of improved white-light LED devices, our research provided fundamental data on the quenching and energy transfer processes in phosphor materials, which will allow the rapid development of even more efficient LED phosphors in the future..

# PRESENTATIONS

## International Conference on Solid State Lighting, SPIE Meeting, Denver, Colorado 2004

*Development of New Phosphors for LED Based Illumination*
A.A. Setlur, G. Chandran, D. Hancu, A.M. Srivastava, and E. Radkov

## Meeting of The Electrochemical Society, Honolulu, Hawaii, October 3-8, 2004

*Photoionization and Quenching in $SrSiO_4Eu^{2=}$*
H.A. Comanzo, A.A. Setlur, A.M. Srivastava, P. Schmnidt, B. Wen, and U. Happek

*Photoionization of $Eu^{2+}$ Ions in $Sr(SCN)_2$*
C.Wickleder, B.Wen, and U. Happek

*$Eu^{2+}$ -> $Mn^{2+}$ Energy Transfer in the UV-LED Phosphor $Ca_5(PO_4)_3Cl$*
H.A.Comanzo, A.A. Setlur, A.M. Srivastava, P. Schmidt, B. Wen, and U. Happek

## DOE Solid State Lighting Workshop, February 3-4, 2005, San Diego, CA

*Development of UV-LED Phosphor Coatings for High Efficient Solid State Lighting*
U. Happek and A.A.Setlur

## 2005 Fall Meeting of the Electrochemical Society, Los Angeles, CA.

*Mechanism for persistent luminescence in $Sr_2MgSi_2O_7:Eu^{2+}: Dy^{3+}$*

M.E.Hannah, U. Happek, P.Schmidt, A.A. Setlur, A.M. Srivastava, and H.A. Comanzo

*On the synthesis and luminescence of red LED phosphors based upon garnet hosts*
A.A. Setlur, W.J. Heward, A.M. Srivastava, H.A. Comanzo, G. Chandran, M.V. Shankar, U. Happek

*A new green phosphor for UV-LEDs: $Na_2Gd_2B_2O_7:Ce^{3+},Tb^{3+}$*
A.M. Srivastava, H.A. Comanzo, A.A. Setlur, J.Hughes, U. Happek

**2005 Fall Meeting of the Electrochemical Society, Los Angeles, CA.**

*Experimental elucidation of the mechanism for persistent luminescence in $SrAl_2O_4:Eu^{2+}$ and $SrAl_2O_4:Eu^{2+}$, $Dy^{3+}$.*
A.A. Setlur, A.M. Srivastava, H.A. Comanzo, M.E. Hannah, U. Happek;

**Third Annual DOE Solid State Lighting Program Planning Workshop. Lake Buena Vista, FL, February 1-3, 2006**

*Development of Efficient UV-LED Phosphor Coatings for High Efficiency Solid State Lighting*
U. Happek and A.A.Setlur

**Phosphors Global Summit 2006, March 13-15, 2006, San Diego, CA**

*Phosphor Efficiency, Thermal Quenching, and Lumen Maintenance*
U. Happek

*Thermoluminescene Excitation Measurements of Photoionization in Doped Insulators*
Jay Fleniken, PhD Thesis, The University of Georgia (2004).

*Thermally Stimulated Luminescence Excitation Spectroscopy as a Technique to Measure the Ionization Energy of $Sr(SCN)_2:Eu^{2+}$*
B. Wen, Master's Thesis, The University of Georgia (2004).

*On the relationship between emission color and $Ce^{3+}$ concentration in garnet phosphors.*
A.A. Setlur and A.M. Srivastava,submitted to Opt. Mater.

*Crystal chemistry and luminescence of Ce3+ doped $Lu_2CaMg_2(Si,Ge)_3O_{12}$\$ and its use in LED based lighting.*
A.A. Setlur, W.J. Heward, Y. Gao, A.M. Srivastava, R.G. Chandran, and M.V. Shankar, Chem. Mater. v.18, 3314 (2006).

*Spectroscopic evaluation of a white light phosphor forUV-LEDs —$Ca_2NaMg_2V_3O_{12}:Eu^{3+}$*
A. A. Setlur, H. A. Comanzo, A. M. Srivastava, and W. W. Beers,
J. Electrochem. Soc. v.152, H205 (2005).